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DOI: 10.1039/C9CC00455F

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Electrochromism of Fast Photochromic Radical Complexes Forming the Light-Unresponsive Stable Colored Radical Cation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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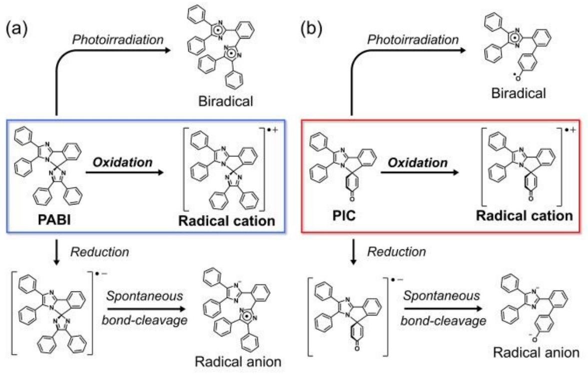
We demonstrated the electrochromism of the photochromic radical complexes containing the triaryl imidazole, fast photoswitchable pentaarylbiimidazole (PABI) and phenoxyl–imidazolyl radical complexes (PIC). The cyclic voltammetry and spectroelectrochemistry revealed that PABI and PIC generate the highly stable radical cation by one-electron oxidation accompanying with the color change from colorless to green. The stability of the radical cation is strongly affected by the dihedral angle between the imidazole ring and the phenyl ring at the 2-position of the imidazole ring.

The molecule that can be switched by one or more external stimuli is an important component for the development of highly elaborate molecular systems.[1-3] Most of the molecular switches are the reversible transformations between two different states by an external stimulus.[4] The combination of several different molecular switches through covalent links has been adopted as a common strategy to achieve multi-responsive molecular systems.[5-7] In contrast, the development of a single molecular switch showing multi-way response to various external stimuli is also demanded to expand the versatility of the design of attractive switching materials. A photochromic molecule is one of the switching molecules that exhibit the reversible isomerization between the colorless and colored states by light irradiation.[8] It has been reported that some of them respond to the other stimuli such as acid/base addition and electric stimulation, and therefore, such photochromic molecules have been accepted as a good candidate for the multi-responsive molecular component.[9-19]

Photochromic hexaarylbiimidazole (HABI) is readily cleaved into a pair of the colored 2,4,5-triphenylimidazolyl radicals (TPIR) upon UV light irradiation and the photogenerated radicals thermally recombine to form the original imidazole dimer.[20,21] We have developed the fast photochromic bridged-imidazole dimers showing the fast thermal recombination reaction by restricting the diffusion of the photogenerated radicals.[22-32] Pentaarylbiimidazole (**PABI**) and phenoxyl-imidazolyl radical complex (**PIC**) are recently developed as novel types of fast photochromic compounds (Scheme 1).[33-36]



Scheme. 1 Photochemical and electrochemical reaction schemes of (a) **PABI** and (b) **PIC**.

Because they are easy to synthesize and to modify appropriate substituents, **PABI** and **PIC** are expected to become attractive fast photochromic frameworks. It has also been known that imidazole dimers show bond cleavage of the C–N bond between the two imidazole rings by the electrochemical reduction. The one-electron reduction of the imidazole dimer leads to the generation of the radical anion which spontaneously breaks the C–N bond forming the imidazolyl radical and the imidazole anion. Although it has been reported that the electrochemical oxidation of the imidazole dimer shows an irreversible oxidation process, the detail of the oxidation process has not been reported to date due to the instability of the radical cation of the imidazole dimer.[37,38] In this study, we investigated the electrochemical oxidation of **PABI** and **PIC** derivatives in detail and revealed the excellent stability of the radical cations of **PABI**

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†Electronic Supplementary Information (ESI) available: [Synthesis, Raman and time resolved spectroscopy experiments, experimental details, the other experimental results.]. See DOI: 10.1039/x0xx00000x

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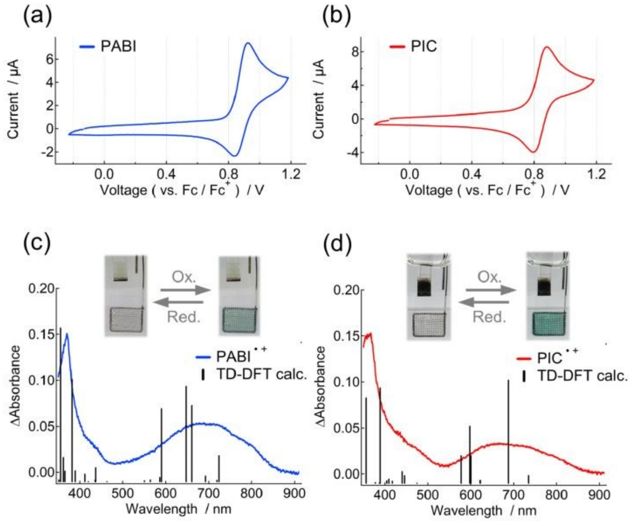

Fig. 1 Cyclic voltammograms of (a) 5.3 mM **PABI** and (b) 6.2 mM **PIC** in acetonitrile containing 0.1 M TBAPF$_6$ as a supporting electrolyte (potential scan rate= 100 mV/s). Spectroelectrochemistry of (c) 1.0 mM **PABI** and (d) 1.0 mM **PIC** under the constant potential at 1.2 V versus Fc/Fc$^+$ in 0.1 M TBAPF$_6$–acetonitrile solution at room temperature and TDDFT calculation results (UMPW1PW91/6-31+G(d,p)//UM052X/6-31(d)). The insets show the corresponding color changes of the solution.

and **PIC**. To the best of our knowledge, this is the first report of the stable radical cation of the photochromic radical complexes containing the triaryl imidazole and the obvious reversible color change by electrochromism.

Fig 1a and 1b show the cyclic voltammograms (CV) for **PABI** and **PIC**, respectively, in acetonitrile with 0.1 M TBAPF$_6$ as a supporting electrolyte. Although the oxidation waves of conventional imidazole dimers are irreversible, the fully reversible oxidation peaks were observed in the case of **PABI** and **PIC**. The half-wave potentials (E$_{1/2}$) were determined to be 0.88 V (versus Fc/Fc$^+$) for **PABI** and 0.84 V (versus Fc/Fc$^+$) for **PIC**. These reversible oxidation reactions indicate the formation of the radical cations (**PABI**$^{\bullet+}$ and **PIC**$^{\bullet+}$) by one-electron oxidation (Scheme 1). So as to reveal the electrochemical oxidation products of **PABI** and **PIC**, we conducted the UV–vis–NIR spectroelectrochemistry as shown in Fig 1c and 1d. The neutral states of **PABI** and **PIC** have no absorption band in the visible light region.[33,35] On the other hand, they absorb a wide range of the visible light under a constant potential at 1.2 V versus Fc/Fc$^+$ at room temperature. Therefore, the drastic color change from colorless to bluish green was reversibly observed by the cyclic voltammetry. The TDDFT calculations for the closed-ring form of **PABI**$^{\bullet+}$ and **PIC**$^{\bullet+}$ were performed at the UMPW1PW91/6-31+G(d,p)//UM052X/6-31G(d) level of the theory. The experimental absorption spectra are in good agreement with the calculation results. The absorption band at around 700 nm can be attributable to the characteristic transition from the HOMO to the SOMO of the radical cation (Fig. S19 and S20). Because the SOMOs of **PABI**$^{\bullet+}$ and **PIC**$^{\bullet+}$ distribute over only the 6π-electron triphenyl imidazole ring, the E$_{1/2}$ values of **PABI**/**PABI**$^{\bullet+}$ and **PIC**/**PIC**$^{\bullet+}$ couples can be estimated to be almost the same value. It has been reported that the C–N bond cleavage of **PABI** and **PIC** was induced by photoirradiation or electrochemical reduction because of the antibonding character of the C–N bond in the LUMO.[33,35] On the other hand, because the HOMOs are not related to the C–N bond formation/dissociation (Fig. S23), **PABI** and **PIC** would not show the electrochemical oxidative bond breaking.

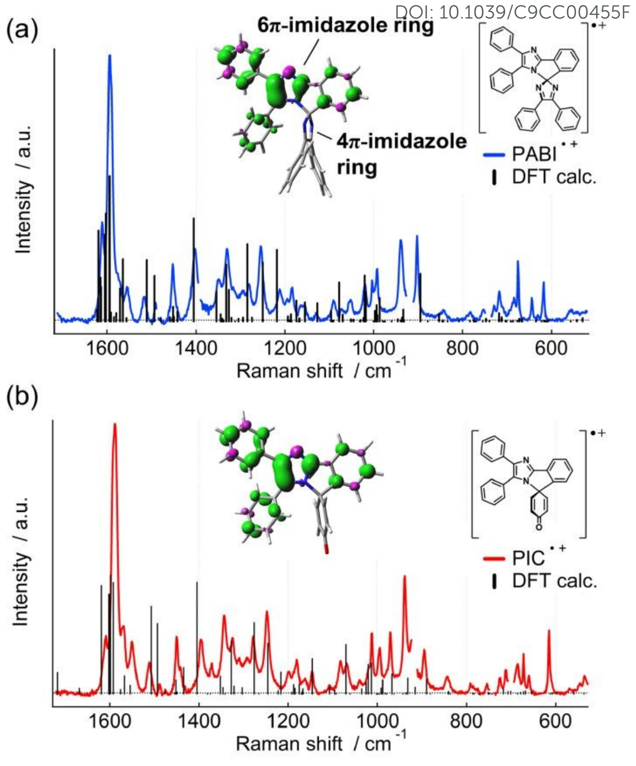

Fig. 2 Resonance Raman spectra of (a) **PABI**$^{\bullet+}$ and (b) **PIC**$^{\bullet+}$ electrochemically generated by the controlled potential coulometry at (a) 1.1 V and (b) 1.2 V versus Fc/Fc$^+$ in the 1.0 mM PABI and PIC solution containing 0.1 M TBAPF$_6$ in acetonitrile (Raman excitation wavelength, 633 nm; power, 6.0 mW; exposure time, (a) 33 min and (b) 60 min) and the DFT calculation results for the radical cations of the closed-ring form (UB3LYP/6-31+G(d,p), scale factor is 0.98). The insets show the spin-density distributions of **PABI**$^{\bullet+}$ and **PIC**$^{\bullet+}$ (UM052X/6-31G(d), isosurface value = 0.003).

The molecular structures of **PABI**$^{\bullet+}$ and **PIC**$^{\bullet+}$ were also investigated in detail by resonance Raman spectroelectrochemistry (RRSE) which is useful to obtain a beneficial information about molecular structures of electrochemical products or intermediates.[39] Fig. 2 shows the resonance Raman spectra of the **PABI** and **PIC** solutions ($\lambda_{ex.}$ = 633 nm) under the constant potential at 1.1 and 1.2 V versus Fc/Fc$^+$, respectively, at room temperature. The radical cations never decomposed through the measurement (Fig. S14). The observed Raman spectra can be well explained with the theoretical non-resonant Raman spectra for the closed-ring form of **PABI**$^{\bullet+}$ and **PIC**$^{\bullet+}$ calculated at the UB3LYP/6-31+G(d,p) level of the theory. We also confirmed that the calculated Raman spectrum of the radical cation of the open-ring form of **PIC** is not consistent with the experimentally obtained Raman spectrum for **PIC**$^{\bullet+}$ (Fig. S16). Particularly, the Raman bands of **PIC**$^{\bullet+}$ at 894, 938 and 971 cm^{-1} are the characteristic bands for

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the closed-ring form. The peaks at 894 and 971 cm^{-1} can be assigned to the vibrational modes originated from the sp^3 carbon (Fig. S15). Thus, the RRSE measurements also suggest that the oxidation of **PABI** and **PIC** does not trigger the C–N bond cleavage reaction. Moreover, we investigated the photochromic reaction of the electrochemically generated **PABI**$^{\bullet+}$ by nanosecond laser flash photolysis. As shown in Fig. S18, the transient absorption signal couldn't be observed by exciting with an intense nanosecond lase pulse. (excitation wavelength, 355 nm; pulse width, 5 ns; power, 6.0 mJ/pulse). Thus, **PABI**$^{\bullet+}$ was found not to show photochromism as observed for **PABI**. It is presumably because the radical cation does not have distinct transitions to the excited states possessing anti-bonding character about the C–N bond.

We investigated the origin of the excellent stability of **PABI**$^{\bullet+}$ and **PIC**$^{\bullet+}$. The spin-density distributions of **PABI**$^{\bullet+}$ and **PIC**$^{\bullet+}$ provide the crucial insight for the stability. The calculated spin-density distribution of each radical cation species is shown in Fig. 2. In both cases, the electron spin density distributes over the 2,4,5-triphenyl imidazole moiety as similar to that of TPIR.[40] TPIR has been well-known as one of the stable radicals because the unpaired spin delocalizes over the three phenyl rings owing to the high planarity of the molecule. Indeed, it has also been reported that the planarity of radical cations plays an important role for the enhancement of the stability.[41,42] Thus, we investigated the relationship between the stability and the planarity of **PIC**$^{\bullet+}$, especially focusing on the dihedral angle between the imidazole ring and the phenyl ring at the 2-position of the imidazole ring of **PIC**. In contrast to the rigid molecular framework of **PIC**, the phenyl ring at the 2-position of the imidazole ring of the reversed phenoxyl-imidazolyl radical complex (**RPIC**) has a degree of freedom of the rotation around the single bond between the imidazole ring and the phenyl ring (Fig.3a).[43,44] Furthermore, the relevant dihedral angle can be modulated by introducing bulky substituents at the ortho positions of the phenyl ring. Based on this idea, we newly synthesized **Me-RPIC** which has two methyl groups at the ortho positions of the phenyl ring (Scheme S1 and Fig. 3a). The imidazole ring and the phenyl ring of **Me-RPIC** are almost orthogonal due to the steric hindrance of the methyl groups (Fig. S8). Thus, we investigated the electrochemical oxidation processes of **PIC2**,[35] **RPIC** and **Me-RPIC**, and the stability of these radical cations.

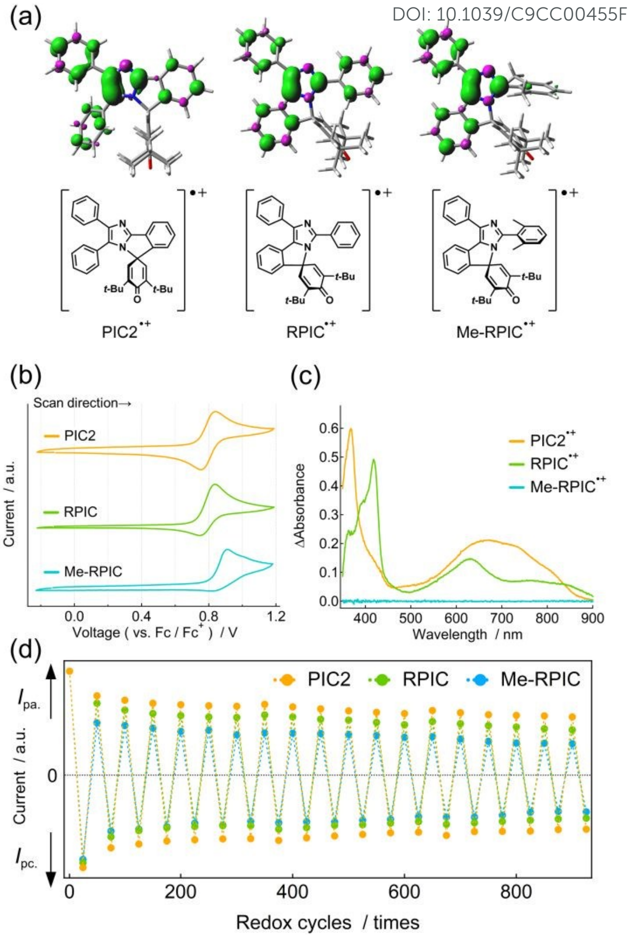

Fig. 3 (a) Molecular structures and spin-density distributions of **PIC2**$^{\bullet+}$, **RPIC**$^{\bullet+}$ and **Me-RPIC**$^{\bullet+}$ (UM052X/6-31G*, isosurface value = 0.003). (b) Cyclic voltammograms and (c) spectroelectrochemistry under the constant potential at 1.2 V versus Fc/Fc$^+$ of 1.0 mM **PIC2**, **RPIC** and **Me-RPIC** in 0.1 M TBAPF$_6$–acetonitrile solution (potential scan rate= 100 mV/s). (d) The change in the anodic ($I_{pa.}$) and cathodic ($I_{pc.}$) peak currents against the redox cycles of **PIC2/PIC2**$^{\bullet+}$, **RPIC/RPIC**$^{\bullet+}$, and **Me-RPIC/Me-RPIC**$^{\bullet+}$ couples in 0.1 M TBAPF$_6$–acetonitrile solution (potential scan rate= 300 mV/s) at room temperature.

Fig. 3a shows the spin-density distributions of these **PIC** radical cations calculated by DFT (UM052X/6-31G(d) level of the theory). Although the unpaired spin of **PIC2**$^{\bullet+}$ and **RPIC**$^{\bullet+}$ distributes over the triphenyl imidazole moiety, that of **Me-RPIC**$^{\bullet+}$ is relatively localized on only the 4,5-diphenyl imidazole moiety. Therefore, it is expected that **Me-RPIC**$^{\bullet+}$ is unstable compared with **PIC2**$^{\bullet+}$ and **RPIC**$^{\bullet+}$. To reveal the reversibility of the electrochromic reactions, we performed the cyclic voltammetry for the three compounds as shown in Fig. 3b. The reversible CV was observed, and the $E_{1/2}$ was determined to be 0.80 V versus Fc/Fc$^+$ for **PIC2**, whereas the CVs for **RPIC** and **Me-RPIC** were not fully reversible when the potential scan rate was 100 mV/s. The irreversible CV of **Me-RPIC** became reversible with increasing the scan rate from 100 mV/s to 1000 mV/s (Fig. S9), indicating that **Me-RPIC**$^{\bullet+}$ decomposed due to the instability before the electrochemical reduction will proceed. Fig. 3c shows the UV–vis–NIR absorption spectra measured by spectroelectrochemistry for **PIC2**$^{\bullet+}$, **RPIC**$^{\bullet+}$, and **Me-RPIC**$^{\bullet+}$ in 0.1 M TBAPF$_6$–acetonitrile solution upon 1.2 V potential application. Unfortunately, the absorption spectrum of **Me-RPIC**$^{\bullet+}$ was not observed because of its instability in this experimental condition. In the cases of **PIC2**$^{\bullet+}$ and **RPIC**$^{\bullet+}$, the absorption bands attributable to the formation of the radical cations appeared in the visible to NIR regions (600 to 850 nm). The durability against the repeated redox cycles of **PIC2/PIC2**$^{\bullet+}$, **RPIC/RPIC**$^{\bullet+}$, and **Me-RPIC/Me-RPIC**$^{\bullet+}$ couples by sweeping the potentials between 0.4 and 1.2 V are shown in Fig. 3d and S10. The anodic ($I_{pa.}$) and cathodic ($I_{pc.}$) peak currents of **Me-RPIC** and **RPIC** significantly decreased during repetitive 900 cycles, whereas **PIC2** shows acceptable durability against hundreds to thousands of the redox cycles. From these results, the dihedral angle between the imidazole ring and the phenyl ring at the 2-

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position of the imidazole ring was found to strongly affect the stability of the radical cation.

In conclusion, we investigated the electrochemical oxidation processes of **PABI** and **PIC**, and revealed that they generate highly stable radical cations, **PABI**$^{\bullet+}$ and **PIC**$^{\bullet+}$, by one-electron oxidation with accompanying the color change from colorless to bluish green. By performing the RRSE measurements, it was revealed for the first time that the photochromic radical complexes containing the triaryl imidazole do not show the C–N bond breaking by electrochemical oxidation. Moreover, by comparing the electrochemistry for **PIC2**, **RPIC** and **Me-RPIC**, we found that the coplanarity between the imidazole ring and the phenyl ring at the 2-position of the imidazole ring is definitely crucial to stabilize the radical cation of the triphenyl imidazole. These findings will give not only a fundamental insight of the electronic structures of the photochromic radical complexes but also a molecular design for the unique photo- and electrochromic materials by using the triaryl imidazole.

Acknowledgment

This work was supported partly by the JSPS KAKENHI Grant Numbers JP18H05263, JP26107010, and JSPS KAKENHI Grant Number JP17K14475 for K.M.

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